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MICRO-SCALE THERMAL ANALYSIS OF ENERGY STORAGE IN CEMENT-BASED COMPOSITES CONTAINING PHASE CHANGE MATERIALS (PCMS)

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Abstract. In the last decades, the use of smart components embedded inside cementitious materials, like Phase Change Material (PCM), has become a more and more attractive solution for saving energy and for providing a more efficient thermal comfortability to modern buildings. Present research running at the Institute of Construction and Building Materials (WiB) of TU-Darmstadt deals with the investigation of advanced coupling of two physical mechanisms represented by a heat problem and microstructural heterogeneities. The thermal response of such a composite system, along with occurring phase change phenomena, will be simulated at the microscale level. A virtual 3D porous microstructure with embedded PCMs, created with the available hydration model Hymostruc, provides a fundamental basis for the analysis of the morphological influence of PCMs on the effective thermal diffusion parameters. The work is aimed at investigating the influence of the morphological effect on the thermal effective properties of hydrating cement combined with Micro-encapsulated (M)-PCMs. Laboratory characterization of the PCMs was performed using a designated test set-up. The thermal performance of cement-based pastes with and without MPCMs were experimentally evaluated and used as benchmark for calibration purposes. Particularly, the obtained results combined with specific heat capacity of PCM-cement pastes and thermal conductivity measurements were taken as reference for validating the proposed numerical technique.

1 INTRODUCTION

In the last century, the use of concrete and/or cementitious-based mortars in structures and buildings has grown towards vast quantities. Since concrete is the most widely used construction material, the reduction of its environmental impact inferred by its production process and use, is an enormous challenge for modern science and technology (Lima et al. 2013). In recent years, the concrete industry widely committed itself to reduce its carbon footprint dramatically, while turning its "grey" image into a "greener" and more environmentally-friendly one (Schneider et al. 2011). However, for enhancing the sectors´ sustainability perspective, a significant effort still has to be done. Main challenges for this are the reduction of its CO_2 footprint, widen its recyclability potential and cutting back on its energy demands (Miller et al. 2016). Advanced technologies in the concrete industry make it possible to go even a step beyond these ambitions, by turning cement-based materials into active thermal energy storing elements (Parameshwaran et al. 2012). Thermal energy can be accumulated in a construction element using sensible, latent and/or thermochemical-based materials. In this context, incorporating Phase Change Materials (PCMs) as thermal energy storage in construction elements turned out to be a very efficient way to level out energy needs in modern buildings and/or other infrastructural applications. Particularly, due to their ability to absorb and liberate large quantities of latent heat, PCMs have the potential to reduce the daily energy demand for heating and cooling, with a positive impact on the global warming and climate change (Pomianowski et al. 2014). Inclusion of PCMs in concrete leads, therefore, to a significant improvement of the materials thermal performance while the efficiency to store thermal heat in a PCM-concrete makes it interesting to investigate the properties that allow for a wider use in construction and building applications (Mehling and Cabeza, 2008).

Several of experimental-based research, available in literature, addressed the hydro-thermo-chemo-mechanical properties of cementitious materials containing PCMs (Cheng et al., 2013; Entrop et al., 2011). Whenever PCMs are embedded in concrete used for passive heat storage in residential buildings, they are characterized by their melting temperature that may vary between 18 °C and 25 °C, which somehow corresponds to a standard temperature range for comfortable living (Kenisarin and Mahkamov, 2016). PCMs employed in concrete can be of organic (paraffin and non-paraffin) and/or inorganic (hydrated salts) nature (Ling and Poon, 2013).

Many theoretical and numerical models are available for simulating heat storage phenomena in porous composites like concrete, mortar, gypsum, etc. Available models developed in the last two decades can be categorized by means of the different scales of observation. Concrete and other cementitious materials are multiphase (composite) materials and, for this reason, it can be considered and modelled as a homogeneous continuum at the macroscale and structural scale, while at lower levels (meso-, micro- and nano-scale) it can be handled as an inhomogeneous multiphase composite. More specifically, structural-scale models allow to capture the essence of heat storage phenomena at the structural (building physics) scale level (Heim and Clarke, 2004). The major objective of these formulations is to build up simplified methods, sometime practice-oriented, for predicting the temperature fluctuations and thermal comfort in a certain construction (Evola et al. 2013; 2014). Macro-scale models are based on the assumption that the schematized material acts as a continuum and homogenous medium. Most classical examples in this field are those related to the use of the so-called Enthalpy-based Method (EM), the Apparent Calorific Capacity Method (ACCM) and the Heat Source Method (HSM) for macroscopic analysis of cementitious composites.

Examples are from Pasupathy et al. (2008a; 2008b), who analyzed the thermal performance of building roofs with PCMs.

A better understanding of PCM mechanics subjected to external thermal fluctuations can be obtained by considering lower scales of analysis (i.e., mesoscale behavior of PCM composite materials). The mesoscale of concrete can be idealized by considering different phases which together constitute such a composite. Thereby, the interaction among the different phases of the composite (i.e., matrix, coarse aggregates, PCMs and interfaces between them) is explicitly considered in these approaches. Even though, nowadays only a few approaches are currently available in literature for modeling meso-scale systems that account for phase changes in concrete (Agauyo et al. 2016).

After the above literature review, Section 2 outlines the experimental plan whose data were employed for validating the numerical models proposed in this article. Then, in Section 3, a discussion is addressed focusing on the numerical approach employed for modelling phase change effects in cementitious pastes. The experimental results of Section 2 are considered in Section 4 to validate the proposed model and demonstrate its ability in simulating the behavior of hardening cement paste with and without PCM. Then, Section 5 will focus on reporting a modelling procedure for cementitious paste composites enclosing PCMs, based on a microscale scale approach and 3D microstructures with different porosities and pore morphologies generated using the Hymostruc model. Finally, concluding remarks and an outline of future research steps to cover the observed research gap on numerical simulations of phase change materials and processes in PCM-cementitious composites will be reported in Section 6.

2 EXPERIMENTAL RESULTS

This section summarizes the experimental results which are considered as a benchmark for the comparison of the experimental results and the corresponding numerical simulations.

2.1 Outline of experimental tests

Experimental data, characterizing the heat storage performance of three different cement pastes with and without PCMs, was obtained from temperature measurements conducted at the WiB laboratory of TU-Darmstadt.

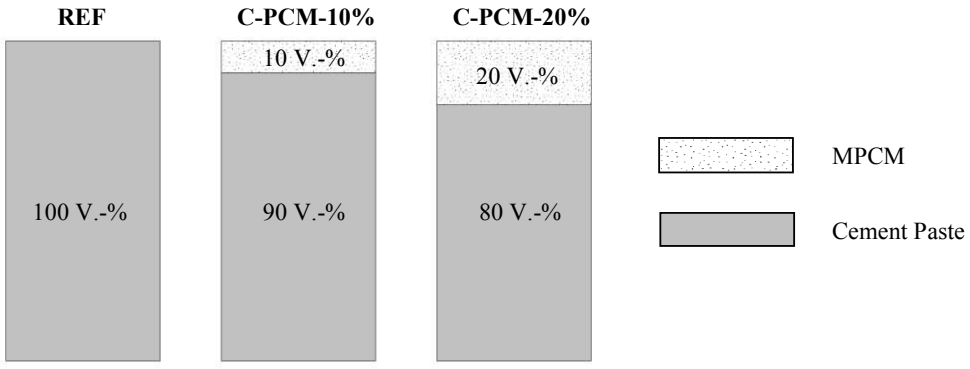


Figure 1: Volumetric composition of the three mixtures.

Particularly, three mixtures were considered with cement type CEM I 42.5 R and a w/c ratio of 0.5 (Table 1). In addition, Micronal® DS 5008 X (BASF, 2013) PCMs were used in this study of which their thermal and physical properties are summarized in Table 2. Table 3

reports detailed information about the ‘‘reference” (REF) cement paste composition, which was kept unchanged in the further two PCM mixtures, i.e., (i) C-PCM-10% mixture made with 10 % in volume of Microencapsulated-PCM (MPCM) and (ii) C-PCM-20% mixture made with 20 % in volume of MPCM (Figure 1).

Cement	Type	Strength after 2 d [MPa]	Strength after 28 d [MPa]		Apparent density [approx. in kg/m^3]	Density [approx. in kg/m^3]
Portland cement	CEM I 42,5 R	>20	≥ 42,5	≤ 62,5	900 – 1200	3100

Table 1: Overview properties of the cement CEM I 42,5 R

PCM	Type	T_m [approx. °C]	Storage capacity [approx. in kJ/kg]	Latent heat capacity [approx. in kJ/kg]	Apparent density [approx. in kg/m^3]	Density [approx. in kg/m^3]
Micronal® DS 5008 X	Powder	26	145	110	250 – 350	900

Table 2: Overview thermo-physical properties of the MPCM employed in this study.

Component	**REF**	**C-PCM-10%**	**C-PCM-20%**
Cement	1215.7 kg/m^3	1173.6 kg/m^3	1131.5 kg/m^3
Water	607.8 kg/m^3	586.8 kg/m^3	565.8 kg/m^3
MPCM	0	90.0 kg/m^3	180.0 kg/m^3
w/c ratio	0.5	0.5	0.5

Table 3: Overview of mix proportions of the three mixtures.

A set of temperature measurements during time were carried out on different samples and in different positions. Figure 2 shows the experimental specimen and positions of the thermocouples employed for experimental validations. The temperature evolutions are measured in 5 positions, lined up in the specimens with sample dimension of 40×40×160 mm (Figure 2a-b). In addition, a semi-adiabatic test set-up was employed to measure, for each 28-day cured sample, the temperature evolution against the increasing temperature condition, imposed through an oven (Figure 3). To this end, the dried specimen where cooled down to an initial temperature of 4.5 °C after which they placed in the test setup end subsequently positioned in the oven with a fixed isothermal temperature of 48° C. This adaptive system with controlled thermal boundary conditions didn´t allow for a heat liberation to the surroundings, because of the insulated boundaries, and was, therefore, predominantly

controlled by the non-insulated surface of the specimen (Figure 3c).

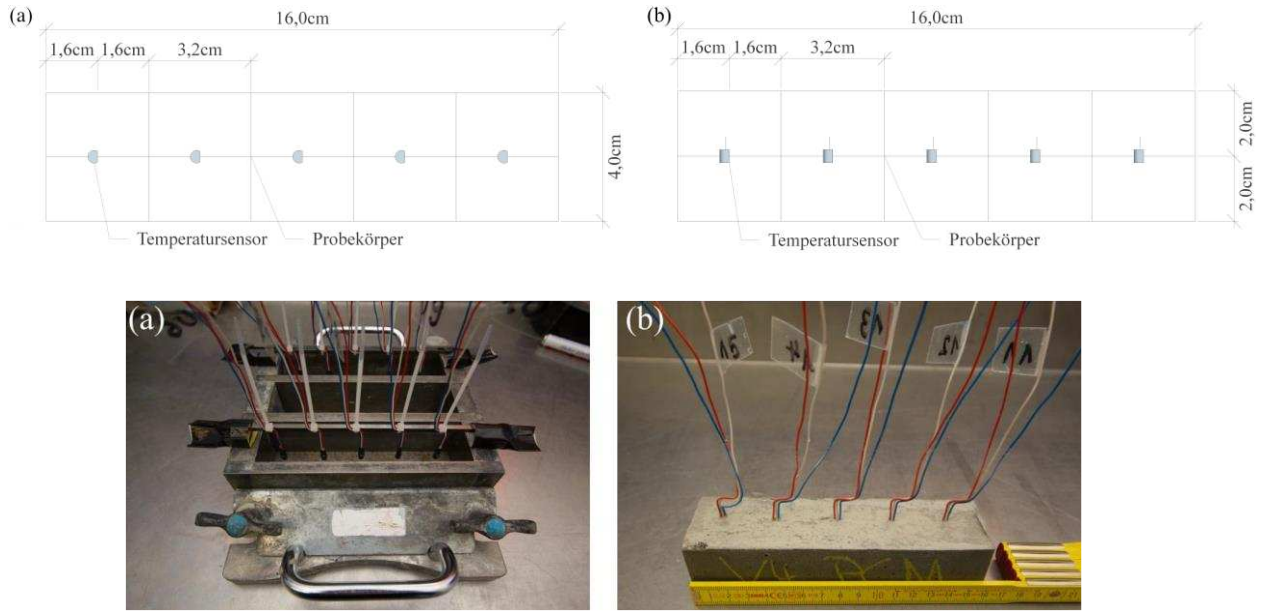


Figure 2: Details of the specimen geometry and position of the 5 thermocouples.

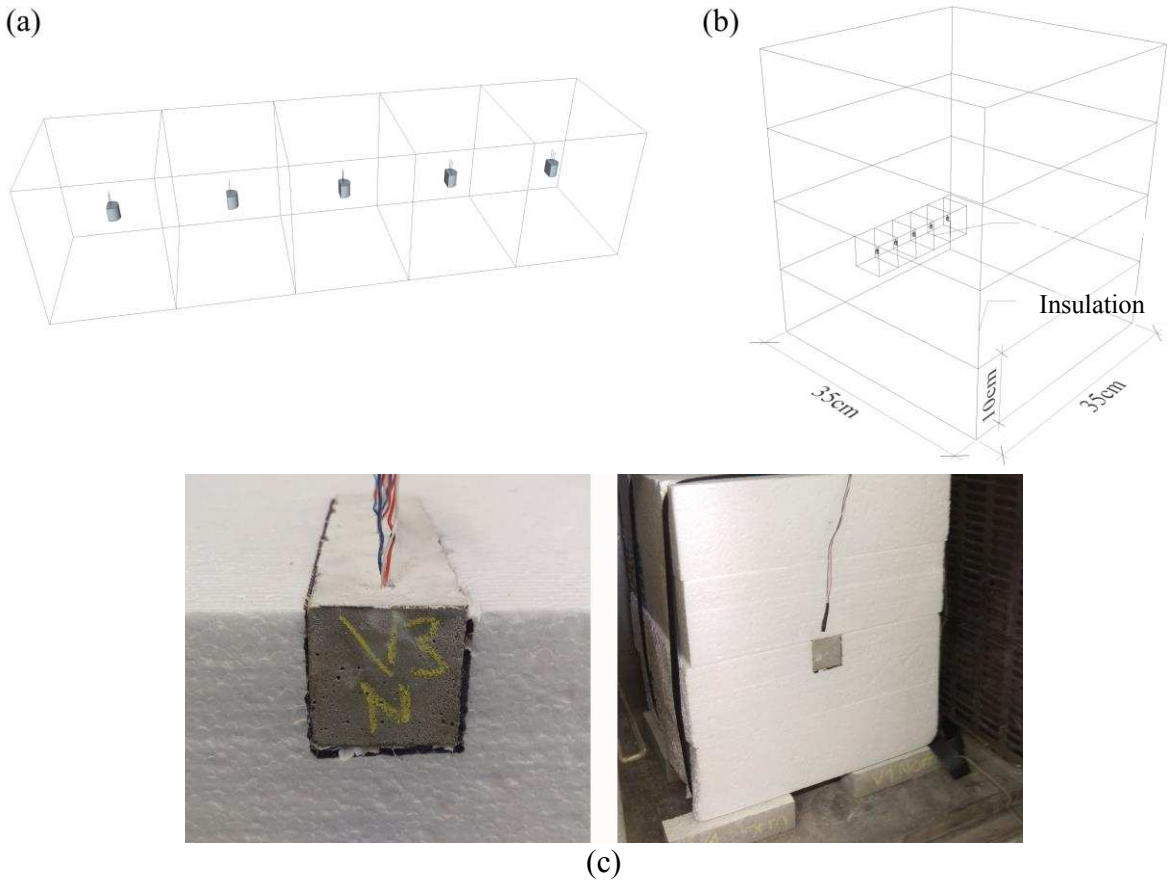
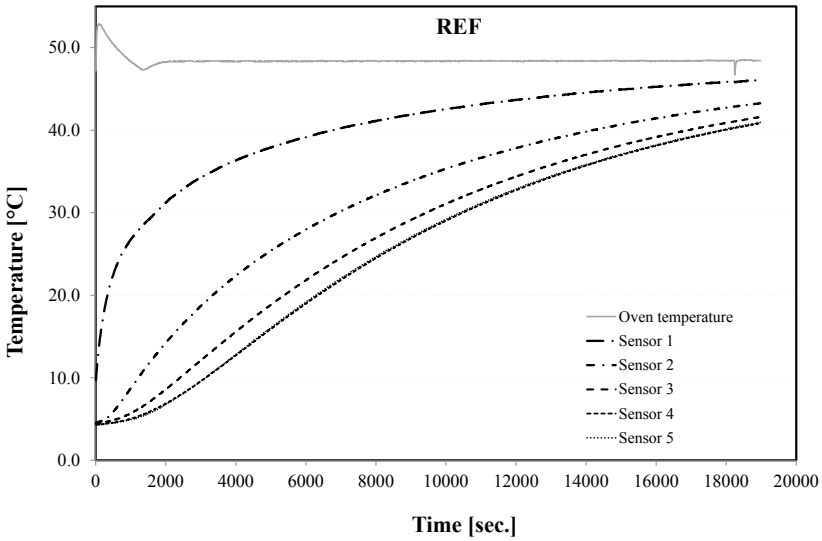


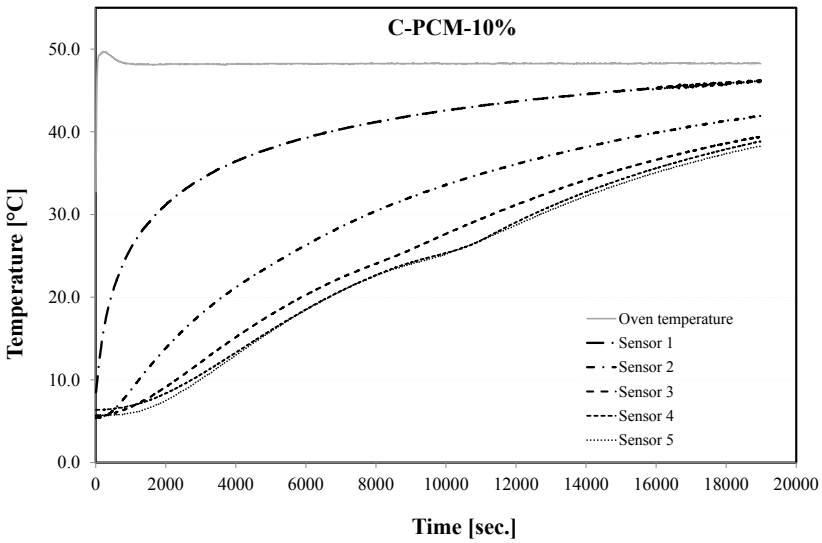
Figure 3: (a) Arrangement of the temperature sensors inside the specimen, (b) 3D view of the sample and the surrounding insulation and (c) detail of the setup with the sample surface free of insulation.

2.2 Experimental results

Figure 4 shows the temperature evolution with time in the specimens, measured for the three different mixtures (Table 3) and conditions described above. The results indicate that the presence of PCM actually decreases the temperature distribution when compared with the REF specimen. The results demonstrate the efficiency of incorporating PCMs as a thermal energy storage material in a construction element. It shows a very practical way to balance energy needs and surpluses in modern buildings and/or in infrastructural applications. From the Figure 4a to c it can be observed how the imposed external heat progresses into the specimen and how the PCMs respond to it. The "dragging" impact of the PCMs changing phase from solid to liquid becomes most pronounced when comparing Figure 4a with Figure 4c, which contains the highest percentage of PCMs. Therefore, with this first approach it can be stated that the inclusion of PCMs in cement pastes alters its thermal performance.



(a)



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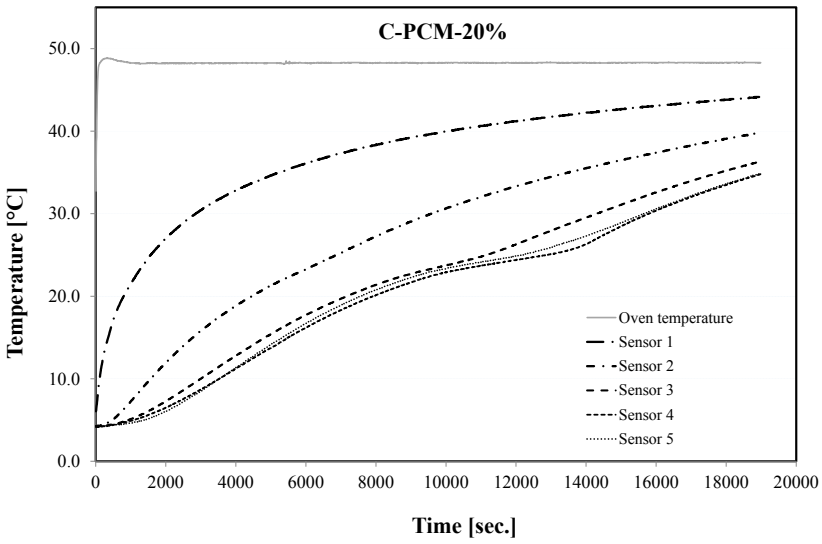

(c)

Figure 4: Experimental results: time evolution of temperature for (a) REF (b) C-PCM-10% and (c) C-PCM-20%.

3 ENTHALPY METHOD AND ACCM APPROACH

The model adopted in this article is based on the assumption that the applied cementitious material can be considered as a continuum and a homogenous medium. As outlined in literature, the fixed grid method is the simplest way to solve thermal problems involving phase changes, which is why it was adopted this work as well. Particularly, the ACCM method for macroscopic analysis of cementitious composites was developed as a standard technique for finite element methods.

The numerical approach for PCM systems can be limited to a conduction problem only as this is the most predominant mechanism for building physics problems in cement-based composites. From this, the basic equation for heat conduction is written as follows:

$$\frac{\partial H}{\partial t} = \nabla.\left(\lambda \nabla T\right) + \dot{q}_v \qquad \forall \mathbf{x} \in \Omega \tag{1}$$

where H is the enthalpy of the system, t is time, $\lambda = \lambda(T, \mathbf{x})$ is the thermal conductivity of the material depending on temperature T, $\mathbf{x}$ is the position vector (of the considered body Ω), $\dot{q}_v$ the source term while $\nabla.$ and ∇ are the divergence and gradient tensorial operators.

The Apparent Calorific Capacity Method (ACCM) takes into account the effect of enthalpy (and its evolution in time) by considering an apparent (or sometime called effective) heat capacity during a thermal phase change. The approach is based on following relationship:

$$\frac{\partial H}{\partial t} = \frac{\partial H}{\partial T}\frac{\partial T}{\partial t}. \tag{2}$$

Furthermore, by introducing the so-called temperature-dependent apparent (effective) heat capacity, defined as $\frac{\partial H}{\partial T} = \rho C_{eff}(T)$, into Eq. (1), the problem modifies into the following relationship:

$$\rho C_{eff}(T)\frac{dT}{dt} = \nabla.\left(\lambda \nabla T\right) + \dot{q}_v \qquad \forall \mathbf{x} \in \Omega. \tag{3}$$

In Eq. (3), temperature is the only variable which needs to be solved and the problem mainly deals with a classical non-linear heat transfer equation. The key novelty of this method is to achieve a proper representation of the apparent specific heat capacity C_{eff} of the material under consideration. In this approach, the apparent calorific capacity for the phase change processes was calculated from interpolated tabular data obtained from the accompanying experimental program conducted in this study.

To complete the problem statement of Eq. (3), the following Initial (I) and Boundary Conditions (BC) have to be considered:

IC:
$$T(\mathbf{x}, t=0) = T_0(\mathbf{x}) \qquad \forall \mathbf{x} \in \Omega \tag{4}$$

and

BC:
$$\begin{aligned} T(\mathbf{x},t) &= T_D && \forall \mathbf{x} \in \Gamma_T \\ (\lambda \nabla T)\cdot \mathbf{n} &= q && \forall \mathbf{x} \in \Gamma_q \\ (\lambda \nabla T)\cdot \mathbf{n} &= h(T_\infty - T) && \forall \mathbf{x} \in \Gamma_c \end{aligned} \tag{5}$$

where Γ_T, Γ_q and Γ_c are the boundaries of domain Ω, where the essential (Dirichlet) and natural boundary conditions are imposed, T_D is the specified temperature, q is the flux, h is the heat convection coefficient and T_∞ is the environmental temperature.

4 NUMERICAL SIMULATION AND COMPARISON

To validate the numerical procedure of the proposed enthalpy-based heat flow model, semi-adiabatic temperature evolutions were simulated and compared with the experimental data reported in Section 2. The set of differential equations described in Section 3 have been solved numerically through the Finite Element Method (FEM). Particularly, the partial differential equation of Eq. (3), which describes the heat-diffusion process throughout the hardening specimens, was solved under a 1D hypothesis, while the space domain was subdivided in n_s spaces (trusses elements), n_s+1 nodes, and, applying a full-implicit Euler Method for solving the transient problem. The initial conditions was imposed following Eq. (4), while the thermo-couples 1 and 5 of the experimental tests were chosen as the essential (Dirichlet) boundary conditions of the numerical system.

Numerical parameters	REF	C-PCM-10%	C-PCM-20%
ρ [kg/m^3]	1617.19	1464.06	1388.67
C_{eff} [J/g K]	1.23	Figure 5a	Figure 5 b
λ [W/m K]	0.586	0.477	0.437
α_f	1.88	2.48	2.94
Number of elements	200		
Number of time steps	1000		

Table 4: Overview of the numerical parameters assumed for the three mixtures.

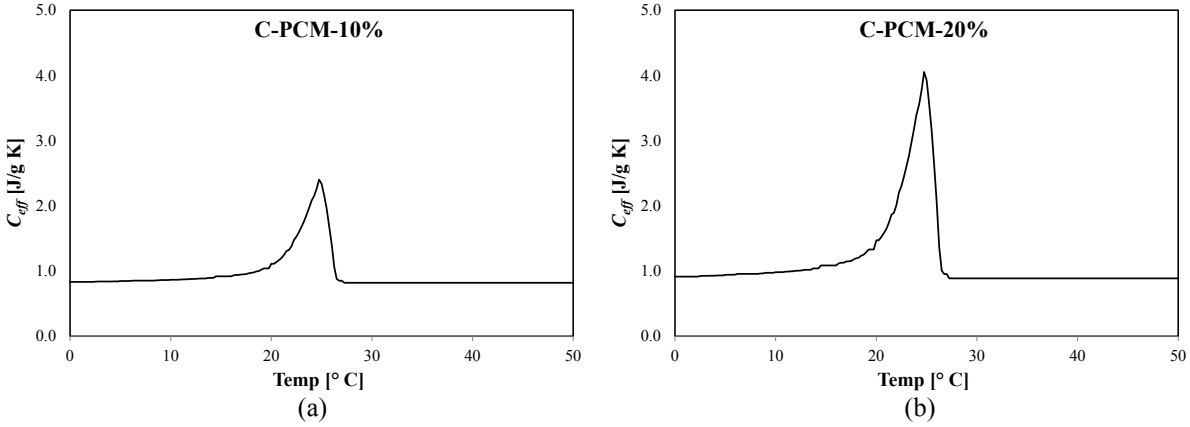

Figure 5: $C_{eff}-T$ curves for (a) C-PCM-10% and (b) C-PCM-20%.

Cement and PCM-cement paste mixtures were simulated with the proposed flow model using the input values outlined in Table 4. It may be worth to mention that a calibrated factor (α_f) was considered for amplifying the thermal conductivity of the system (due to its own non-adiabatic nature), employed for the experimental data simulations. The results are plotted in Figure 6 to Figure 8, and it can be observed that the model reproduces very similar temperature evolutions as measured experimentally. The potential of the proposed model to simulate the temperature evolutions of the mixture with increasing amounts of PCM (e.g., C-PCM-10% and C-PCM-20% mixtures), with just using the experimentally obtained C_{eff} curves turned out to be very promising in this first stage of the analyses.

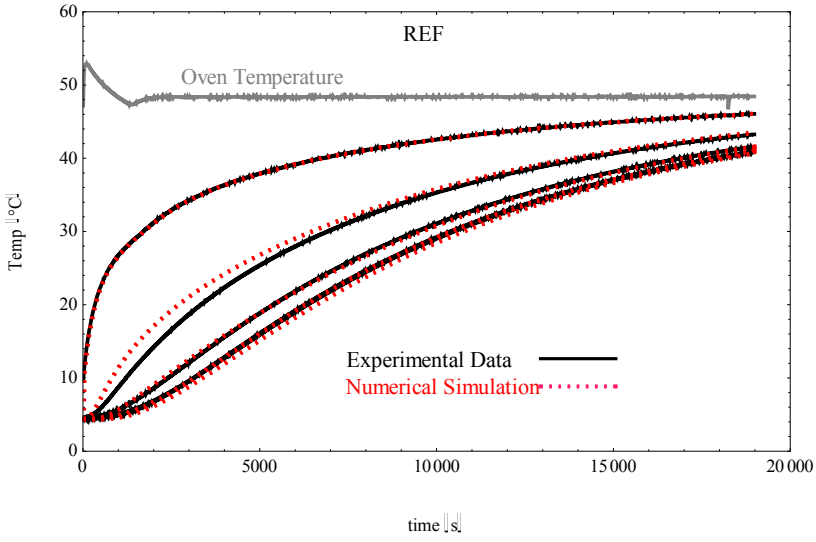

Figure 6: Experimental vs. Numerical results: Temperature evolution of the REF mixture.

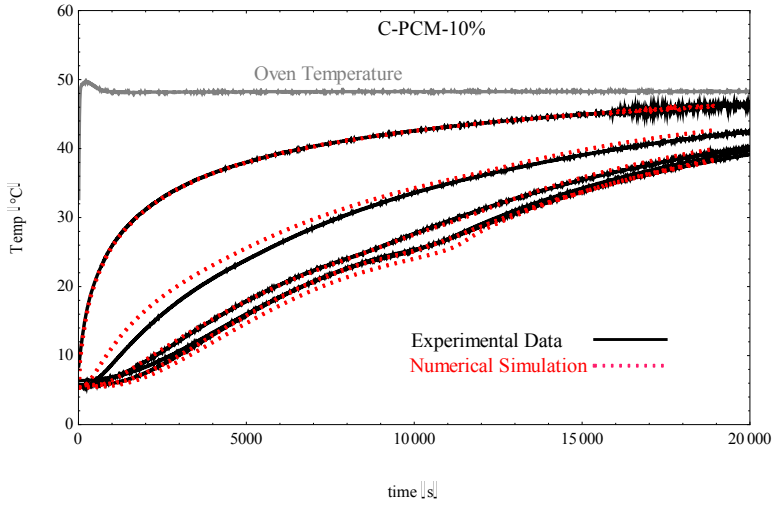

Figure 7: Experimental vs. Numerical results: Temperature evolution of the C-PCM-10% mixture.

The temperature curves of the REF specimen (without PCM) show the upper boundary values of the temperature evolution, whereas the temperature measurements in specimens having 10% and 20% of PCM volume fraction show a decrementing temperature evolution as a result of the energy storages due the phase change, occurring inside the cement-based composites. This trend can be clearly observed when comparing the results of the C-PCM-20% mixture with the C-PCM-10% one, which is more pronounced for higher amounts of PCMs. The impact of PCMs was also very well captured by the proposed numerical simulations.

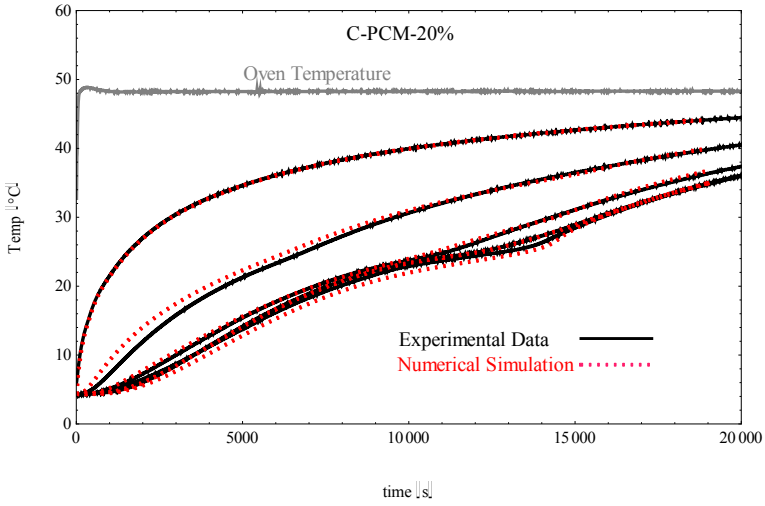

Figure 8: Experimental vs. Numerical results: Temperature evolution of the C-PCM-20% mixture.

5 ENERGY STORAGE AND 3D MICROSTRUCTURAL ANALYSIS

This section addresses a numerical modeling approach of heat transport in hydrated cement pastes containing PCMs. The section only reports a plan for future investigations and shows potential research lines based on the use of virtual three-dimensional (3D) microstructures with different porosities, pore morphologies and distribution of microencapsulated PCMs.

5.1 3D Microstructure

In the current article, the hydration model Hymostruc (Breugel 1991; Koenders, 1997) is employed, to determine a 3D virtual PCM-cement paste microstructure as function of the random spatial configuration of cement particles in a predefined REV, the degree of hydration, both particle size distributions of cement and MPCM (Figure 9), chemical composition of the cement, morphological development, water-to-cement ratio and the reaction temperature.

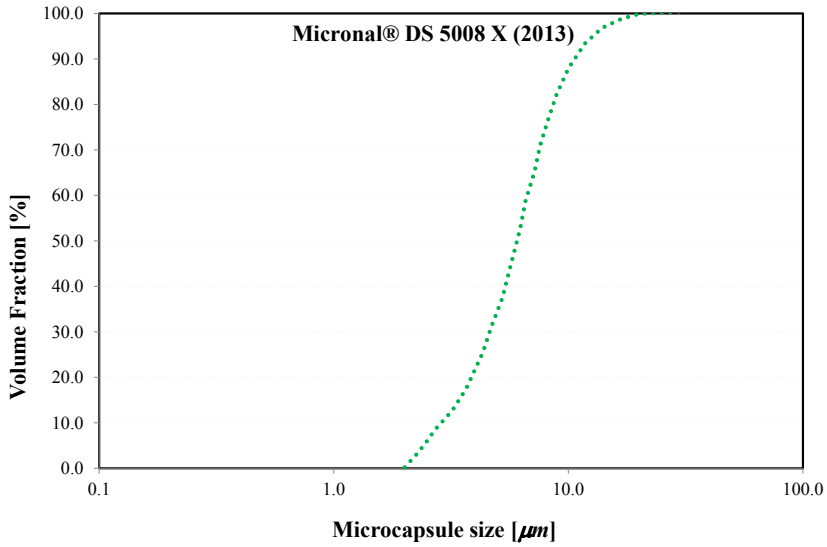

Figure 9: MPCM size distribution of Micronal® DS 5008 X (BASF, 2013).

(a) (b) (c)

Figure 10: 3D simulated microstructure: (a) initial anhydrated cement and MPCM particles, (b) only MPCMs and (c) configuration after the hydration.

The w/c ratio is the principal parameter that controls the morphology of the porous microstructure (Ukrainczyk and Koenders, 2014). Thus, the effect of the porosity and pore complexity as well as the MPCM volume fraction and its dependency towards the RVE size has to be evaluated with respect to the resulting thermal energy storage performance of the composite. The REV shown in Figure 10, is characterized by a 3D virtual microstructure that has a cubic shape with a rib size of 100 μm, a regular Portland cement with a specific surface of 400 $m^2.kg^{-1}$, a water-to-cement mass ratio of w/c = 0.45, an isothermal reaction temperature of 20°C and a MPCM volume fraction of 10% with a particle distribution

highlighted in Figure 9 and Figure 10b. The initial state (un-hydrated) of the microstructures is determined by cement particles that follow a predefined distribution (Figure 10a). Particularly, particles are stacked based on a random selection of locations with an equal probability of occurrence, where placing of the particles starts from the largest particles down to the smaller ones. The process continues until all particles in the smallest fractions have been stacked. Periodic boundary conditions are applied. After having generated this initial particle structure (Figure 10a), hydration algorithms are invoked for simulating the hydration evolution of the particles and the associated expansion of the outer shells of hydration products, whilst forming a 3D virtual microstructure (Figure 10c).

5.2 Homogenized heat energy storage properties

The diffusion-type heat flow in a cementitious composite can be described according to the following differential equation:

$$\frac{dT}{dt} = \nabla.\left(D_j \nabla T\right) \tag{6}$$

where $D_j(T) = \dfrac{\lambda}{\rho C_{eff}(T)}$ is the thermal diffusivity of the jth micro-component (pore, hydration products, anhydrate cement grain and MPCMs.

At the homogenized length scale, the diffusion transport model of Eq. (6) can be written as follows:

$$\frac{d\bar{T}}{dt} = D_{\text{hom}} \nabla^2 \bar{T} \tag{7}$$

where $\bar{T}$ is the average temperature of the diffusing micro-phases, D_{hom} the effective macroscopic diffusivity in a porous media and ∇^2 is the Laplace operator.

By solving Eq. (6) it is possible to define the mean value of the temperature $\bar{T}_{\mathbf{n}j}$ throughout the faces (- and +) and in the mean layer (×) of the REV:

$$\bar{T}^{-}_{\mathbf{n}j} = \frac{1}{A}\int_{\Gamma^{-}_{\mathbf{n}j}} T\, d\Gamma^{-}_{\mathbf{n}_j} \qquad \bar{T}^{\times}_{\mathbf{n}j} = \frac{1}{A}\int_{\Gamma^{\times}_{\mathbf{n}j}} T\, d\Gamma^{\times}_{\mathbf{n}_j} \qquad \bar{T}^{+}_{\mathbf{n}_j} = \frac{1}{A}\int_{\Gamma^{+}_{\mathbf{n}j}} T\, d\Gamma^{+}_{\mathbf{n}j} \qquad j=x,y,z. \tag{8}$$

Thus, by using a backward difference scheme at time $^{n+1}$ and a second-order central difference approach for the space derivative in the x-, y- and z-directions, Eq. (7) can be used for evaluating the D_{hom} as follows:

$$D_{\text{hom},j} = \frac{\dfrac{{}^{n+1}\bar{T}^{\times}_{\mathbf{n}j} - {}^{n}\bar{T}^{\times}_{\mathbf{n}j}}{\Delta t}}{\dfrac{{}^{n+1}\bar{T}^{+}_{\mathbf{n}j} - 2\,{}^{n+1}\bar{T}^{\times}_{\mathbf{n}j} + {}^{n+1}\bar{T}^{-}_{\mathbf{n}j}}{\Delta L_j^2}} \qquad j=x,y,z \tag{9}$$

where Δt is the time step and ΔL_j (with $j=x,y,z$) is based on the REV dimension. Finally, the homogenized diffusivity can be evaluated as follows:

$$D_{\text{hom}} = \frac{D_{\text{hom},x} + D_{\text{hom},y} + D_{\text{hom},z}}{3}. \tag{10}$$

5.3 Statistical evaluation of RVE

The study of Representative Element Volume (REV) of heterogeneous PCM-cement paste

microstructures will be aiming at defining the minimum size of a sample that must employed for determining the corresponding effective properties of a homogenized macroscopic model. The REV dimension should be large enough to contain the necessary information about the microstructure in order to be representative. An indicator proposed by (Guittman et al., 2006) can be estimated for each 3D microstructure to find out the most appropriate REV size and particularly to quantify the change of the calculated homogenized (effective) thermal property based on the mean value calculated for the different numerical realizations. More specifically, six different generations of the initial cement particle locations needs to be generated and used for the hydration simulation and for each different mixture type.

The following expression was proposed by Guittman et al. (2006)

$$\chi^2 = \sum_{i=1}^{m} \left(R_{\text{Diff,i}} - R_{\text{Diff,a}} \right)^2 / R_{\text{Diff,a}}{}^2 \tag{11}$$

where $R_{\text{Diff,i}}$ is the investigated effective parameter (i.e., the thermal diffusivity), $R_{\text{Diff,a}}$ is the average of the investigated $R_{\text{Diff,i}}$, and $m=6$ the total number of numerical realizations performed with different initial cement particle and MPCM locations.

The variability of the results can be estimated with χ^2, indicating that for smaller values of χ-*square*, the closer the volume of the sample under consideration represents the expected REV. In fact, the true REV may only be obtained for a sample with an infinite volume. Nonetheless, a smaller size of a sample can normally be used if the value of χ^2 is acceptably low. Generally, 0.1 is regarded to be an acceptable value (Zhang et al., 2010).

6 CONCLUDING REMARKS

The actual paper proposes a theoretical model for simulating the thermal behavior in hardened cement paste with and without Microencapsulated-PCM. A FEM-based approach formulated in the framework of the Enthalpy method where the Apparent Calorific Capacity Method (ACCM) was solved to accurately analyze the above mentioned phenomena. The model was validated by means of temperature curves measured from three different cement pastes without MPCMs and with 10% and 20% in MPCM volume fraction contents. The main aim of this validation was to demonstrate the potential of the proposed method to simulate the experimental test responses for given boundary and initial conditions. For the selected mixtures, good agreement was found between measured and simulated temperatures.

The proposed ACCM based flow model was developed within the framework of the "2CENENRGY" project and should be considered as a first approach towards the design of an analysis tool for cement pastes with MPCMs at lower scales of observations such as micro (poroscale) and meso-scale. The model will be further developed in this respect with emphasis on investigating the 3D thermal-mechanical response in microscopic specimens.

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